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(71) Applicant: NGK INSULATORS, LTD.
2-56, Suda-cho, Mizuho-ku
Nagoya-shi, Aichi 467(JP)

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(72) Inventor: Nishizawa, Hitoshi Iwakura-Danchi
1 Nakaura Higashishin-Machi
Iwakura City Aichi Pref.(JP)
Inventor: Shibata, Kazuyoshi NGK
Minami-Kazoku Apartments
15 Takeda-Cho 2-Chome Mizuho-Ku
Nagoya City Aichi Pref.(JP)

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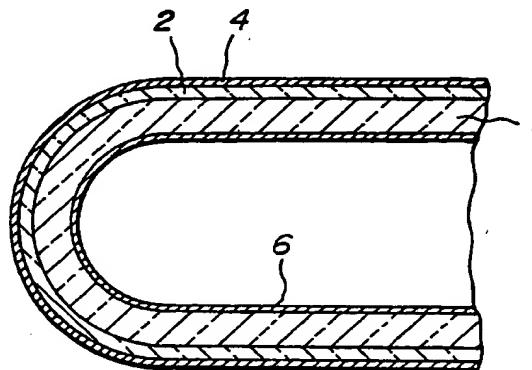
(74) Representative: Paget, Hugh Charles Edward
et al
MEWBURN ELLIS & CO. 2/3 Cursitor Street
London EC4A 1BQ(GB)

(54) Electrochemical elements.

(57) An electrochemical element comprises a solid electrolyte (1,2) and a pair of electrodes (4,6) provided in contact with the solid electrolyte. To achieve good operation at low temperature, and good response and durability, the solid electrolyte consists of a dense solid electrolyte body (1) and a porous solid electrolyte layer (2). At least one of the electrodes is a cermet electrode (4) which is formed in contact with the porous solid electrolyte layer (2), being fired simultaneously with the dense solid electrolyte body (1) and the porous solid electrolyte layer (2). The first electrode may be exposed, through a diffusion-resisting means, to a space for a gas to be measured.

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FIG. 1



ELECTROCHEMICAL ELEMENTS

The present invention relates to electrochemical elements. More particularly, the invention relates to electrochemical elements to be used for controlling combustion of automobile engines or controlling combustion in a variety of industrial furnaces. The invention is specifically directed to electrochemical elements having excellent response, operability at low temperatures, and durability.

Heretofore, electrochemical elements which each comprise a dense solid electrolyte and at least a pair of cermet electrodes provided in contact with this dense solid electrolyte and which have been simultaneously fired have been well-known as sensors capable of detecting the concentrations of various gas components in gases to be measured. For instance, sensors for determining the concentration of oxygen according to the principle of oxygen concentration cells with use of a zirconia porcelain as an oxygen ion conductive solid electrolyte have been developed as oxygen sensors for detecting the concentration of oxygen in combustion exhaust gases emitted from automobile engines, or the concentration of oxygen in combustion exhaust gases emitted from industrial furnaces, boilers or the like. As for internal combustion engines or the like, in order to control the air-fuel ratio of a mixed gas generally consisting of air and a fuel to an intended value at a high accuracy, the amount of the fuel to be fed to the internal combustion engine or the like is controlled by detecting the concentration of oxygen in exhaust gases, which concentration has correlation with the air-fuel ratio, with use of the above sensor.

However, when the solid electrolyte and the electrodes are formed by simultaneous firing in electrochemical elements such as the above oxygen sensors, it is very difficult to attain all the features as excellent operability at low temperatures, response, and durability at the same time.

That is, in order to obtain electrochemical elements having excellent durability, the firing needs to be effected at temperatures high enough to sufficiently sinter a dense solid electrolyte body. At that time, cermet electrodes are sintered excessively because the solid electrolyte as its base shrinks during the firing or the sintering of the cermet electrodes is promoted with a flux oozing out from the solid electrolyte body with sintering of the solid electrolyte body. Consequently, it lowers porosity of the electrode layers to lessen an effective area of the electrodes. Thus, this leads to deterioration in operability at low temperatures and response. On the other hand, when the firing temperature is lowered, operability at low temperatures

and response are improved. However, porcelain is not sufficiently sintered, so that durability is deteriorated.

Therefore, the present invention has been accomplished to solve the above mentioned problems.

According to a first aspect of the present invention, there is a provision of an electrochemical element comprising a solid electrolyte and a pair of electrodes provided in contact with the solid electrolyte, the solid electrolyte consisting of a dense solid electrolyte body and a porous solid electrolyte layer, and at least one of a pair of the electrodes being a cermet electrode which is formed in contact with the porous solid electrolyte layer when being fired simultaneously with the dense solid electrolyte body and the porous solid electrolyte layer.

According to a second aspect of the present invention, there is a provision of an electrochemical element comprising a solid electrolyte, and first and second electrodes provided in contact with the solid electrolyte, the first electrode being exposed, through diffusion-resisting means having a preset diffusion resistance, to a space for a gas to be measured, the solid electrolyte consisting of a dense solid electrolyte body and a porous solid electrolyte layer, and at least one of the first and second electrodes being a cermet electrode which is formed in contact with the porous solid electrolyte layer when being fired simultaneously with the dense solid electrolyte body and the porous solid electrolyte layer.

According to the present invention, the porous solid electrolyte layer is interposed between the electrode and the dense solid electrolyte body, and serves to improve activity of the electrode. In addition to the one of the first and second electrodes, another porous solid electrolyte is preferably interposed between the other electrode and the dense solid electrolyte layer.

Further, it is preferable to provide a second dense solid electrolyte body and third and fourth cermet electrodes which are formed in contact with the second dense solid electrolyte through simultaneously sintering them, and to expose the third cermet electrode to substantially the same gas atmosphere as that of the first cermet electrode, whereby a wider range of gases can be measured at higher precision. In this case, a compact structure can be attained by making the first electrode and the third electrode of a single common electrode.

The gas tightness of the dense solid electrolyte body in the present invention has only to be such

that a diffused amount of a gas reaching the first electrode through the dense solid electrolyte body from the space for the exterior gas to be measured is small enough to be ignored as compared with that of the gas reaching the first electrode directly or through the diffusion-resisting means from the space for the gas to be measured. Ordinarily, the solid electrolyte having an open porosity of less than 1% is preferred. On the other hand, since the porous solid electrolyte layer needs to have porosity great enough to not promote sintering of the electrode through simultaneous firing, solid electrolyte having an open porosity of 2 to 50% after the firing is preferred.

These and other optional features and advantages of the present invention will be appreciated upon reading of the invention when taken in conjunction with the attached drawings, with the understanding that some modifications, variations, and changes of the same could be made by the skilled person in the art to which the invention pertains.

For a better understanding of the invention, reference is made to the attached drawings, wherein:

Fig. 1 is a sectional view of an embodiment of the electrochemical element according to the present invention; and

Figs. 2 to 6 are sectional views of other embodiments of the electrochemical elements according to the present invention, respectively.

A process for forming the porous solid electrolyte layer and the dense solid electrolyte body in the present invention will be explained as follows.

First, the porous solid electrolyte layer is formed as follows:

A material as disclosed in Japanese patent application Laid-open No. 60-135,756 which is removed by heating is pulverized, and mixed into a solid electrolyte-forming powdery material in an amount of 15 to 70% by volume, preferably in an amount of 30 to 50% by volume of a total powder, followed by shaping and firing.

Or, a ceramic powder which is capable of being sintered at temperatures higher than that of a solid electrolyte such as alumina is mixed into a solid electrolyte-forming powdery material in an amount of less than 50 molar %, preferably in an amount of 15 to 30 molar % of a total powder, followed by shaping and firing.

Alternatively, while a solid electrolyte material having a lower sintering temperature, for instance, partially stabilized zirconia, is used for a dense solid electrolyte body, a solid electrolyte material having a higher sintering temperature, for instance, fully stabilized zirconia is used for a porous solid electrolyte layer.

Further, the particle size may be varied. For instance, fine powder having a specific surface

area of not less than 15 m²/g is used for the dense solid electrolyte layer and coarse powder having a specific surface area of 10 m²/g for the porous electrolyte layer. Alternatively, a packing density before firing is varied by varying the particle size distribution, for example, by using a high packing density powder consisting of fine powder and coarse powder at the same ratio as the dense solid electrolyte body and only a coarse powder as the porous solid electrolyte layer, respectively, consequently varying the porosity after the firing.

In addition, the porosity after the firing may be varied by using a readily sinterable powder obtained by a dry type milling process as a dense solid electrolyte body and a not easily sinterable powder obtained by a wet type milling process as a porous solid electrolyte layer, respectively, or by varying addition amounts of a sintering aid to be added to the dense solid electrolyte body and the porous solid electrolyte layer.

Further, the above methods may appropriately be combined.

The porous solid electrolyte layer is formed in a filmy fashion on a shaped body giving the dense solid electrolyte body according to a conventional technique such as screen printing, spraying, dipping, transferring or the like by using a liquid or paste of the solid electrolyte material selected from the above methods, an organic binder, a solvent, etc. Alternatively, a green sheet giving a porous solid electrolyte layer is formed according to a doctor blade process or the like, and press adhered to a green sheet giving a dense solid electrolyte under heating, which is then simultaneously fired.

As an ion-conductive solid electrolyte used in the present invention, conventional materials, for instance, zirconia porcelain, Bi₂O₃-Y₂O₃ base solid solution, etc. as an oxygen-ion conductor, SrCe_{0.85}Yb_{0.05}O₃ as a proton conductor, CaF₂ as halogen-ion conductor may be used.

The cermet electrode preferably used in the present invention is formed by mixing a powder of a platinum group metal such as platinum, rhodium, palladium, iridium, ruthenium or osmium, or a metal such as gold or nickel with a ceramic powder such as zirconia, yttria or alumina such that the metallic powder accounts for not less than 40% by volume, preferably from 60 to 80% by volume of the entire powder, adding an organic binder, a solvent, etc. to the mixture to obtain a liquid or pasty preparation, forming a film of the thus obtained mixture on a shaped body giving the dense solid electrolyte body or the porous solid electrolyte layer according to screen printing, spraying, dipping, transferring or the like, and simultaneously firing it with the latter.

As the electrodes in the present invention, besides the cermet electrode, an electrode formed by

a conventional technique such as sputtering, ion plating, plating, vapor deposition or the like after the firing the solid electrolyte body may be used as a part of the electrodes.

As the diffusion-resisting means in the present invention, a porous ceramic layer, pin holes, a narrow flat space, or an appropriate combination thereof may be used. When the porous ceramic layer is used, it is preferable to form this layer by firing simultaneously with the solid electrolyte, the cermet electrodes, etc. The porous ceramic layer may be formed by mixing a ceramic material such as alumina, zirconia, spinel, or magnesia, or a mixture thereof; and if need be, the above material which is removed by heating, with an organic binder, a solvent, etc. to obtain a liquid or pasty preparation, and forming a film on a shaped body giving the dense solid electrolyte from the above preparation according to a conventional technique such as screen printing, spraying, dipping, transferring or the like. Alternatively, the porous ceramic layer may be formed by forming a green sheet according to a doctor blade process, press adhering it to a green sheet giving the dense solid electrolyte under heating, and firing them simultaneously.

When the electrochemical element according to the present invention is used as an electrochemically pumping cell, porosity inside an electrode layer increases to lower a diffusion resistance. Thus, the solid electrolyte in contact with the negative electrode is less deteriorated through being reduced due to extreme drop in the concentration of oxygen near the electrode. However, this has the merit that even if the solid electrolyte is deteriorated, the solid electrolyte is restored more speedily as compared with the dense solid electrolyte body.

In the following, embodiments according to the present invention will be explained in more detail with reference to the attached drawings, and the construction of the present invention will more specifically be made clearer.

Fig. 1 shows a sectional view of an oxygen sensor as an embodiment of the electrochemical element according to the present invention.

A porous solid electrolyte layer 2 and then a first electrode 4 are successively coated on an outer surface of a bottom-closed cylindrical dense solid electrolyte body 1 made of partially stabilized zirconia, and they are integrally fired. On the other hand, a second electrode 6 is formed on an inner surface of the solid electrolyte body by plating. In this case, the outer surface of the solid electrolyte body 1 is located on a side exposed to a space for a gas to be measured, while the inner surface is located on a side exposed to air as a reference gas. Thereby, a partial pressure of O₂ in the gas to

be measured can be detected based on an electromotive force generated between the first electrode 4 and the second electrode 6 with reference to air.

Fig. 2 shows an embodiment of an oxygen sensor for detecting an O₂ partial pressure in the gas to be measured by utilizing the principle of an oxygen concentration cell as in Fig. 1.

In this sensor, a porous solid electrolyte layer 12, a first electrode 14, and a porous ceramic layer 30 are successively coated on one surface of a planar dense solid electrolyte 10 by a screen printing process, and a second electrode 16 is similarly coated on the other surface. To this laminate are piled and integrated a spacer member 20 with a cut portion for an air passage 18, a lid 22, and electrically insulating ceramic members 26 and 28 holding a heating pattern 24 among them, which is fired to form an electrochemical element.

In this case, since the electrochemical element is heated by applying an electrical current to the heating pattern 24 from an external electric source, an O₂ partial pressure at lower temperatures in a gas to be measured can be detected. The porous ceramic layer 30 is a protective layer to protect the first electrode 14 from materials such as phosphorus, lead, etc. contained in the gas to be measured.

Different from Figs. 1 and 2, Fig. 3 is a sectional view of an oxygen sensor using the electrochemically pumping principle. A porous diffusion layer 48 is formed on the outer side of a first electrode 44 as a diffusion-resisting means. A porous ceramic layer 49 is formed on the outer side of the second electrode as a getter. Reference numerals 40 and 42 denote a dense solid electrolyte body and a porous solid electrolyte layer, respectively.

Namely, when a DC voltage is applied between the first electrode 44 and a second electrode 46 from an external power source, oxygen ions are pumped up from the first electrode 44 toward the second electrode 46 to lower the O₂ concentration near the first electrode 44. At that time, the O₂ concentration in the gas to be measured is detected based on an amount of O₂ diffusing into the first electrode 44 through the porous diffusing layer 48 as the diffusion-resisting means having a preset diffusion resistance.

Fig. 4 is an oxygen sensor based on the electrochemically pumping principle as in Fig. 3. What is different from Fig. 3 are that a second porous solid electrolyte layer 53 is provided between a second electrode 56 and a dense solid electrolyte layer 50 and fourth electrodes 62 are provided inside the dense solid electrolyte 50, opposed to a third electrode (which is united with a first electrode in this embodiment) 54, to form an oxygen

concentration cell, whereby an O₂ partial pressure near the third (first) electrode varying due to the electrochemical pumping between the first (third) electrode 54 and the second electrode 56 is measured. A reference gas atmosphere is formed by effecting fine pumping between the third (first) electrode 54 and the fourth electrodes 62 and pouring oxygen ions into the fourth electrodes 62. The electrically insulating porous ceramic layers 64 are provided to store the above reference gas atmosphere, electrically isolate the second electrode 56 from the fourth electrodes 62, and reduce influences giving the potential of the fourth electrode 62 due to the pumping between the first (third) electrode 54 and the second electrode 56. Reference numerals 52, 58 and 60 are a porous solid electrolyte layer, a porous diffusion layer, and a porous ceramic layer, respectively.

Fig. 5 is an electrochemical element having two sets of electrochemical cells each comprising a solid electrolyte and a pair of electrodes provided in contact with the solid electrolyte. Porous solid electrolyte layers 72, 74, 76 and 78 are provided between each of all electrodes 64, 66, 68 and 70 and a dense solid electrode body 60 or 62, respectively. A flat space 88 to which the first and third electrodes are exposed is a diffusion-resisting means having a preset diffusion resistance, and is communicated, through a gas introduction hole 90, with a space for a gas to be measured. The first and second dense solid electrolyte bodies 60 and 62 are connected and integrated together through a spacer member 61 made of the same material as that of the electrolyte bodies 60 and 62, thereby giving a firm structure.

A ceramic heater layer 92 is buried between lid members (dense solid electrolyte bodies) 82, 84, which enables measurement of gases at lower temperatures.

Reference numerals 86 and 94 denote a porous ceramic layer and an air passage, respectively.

Further, Fig. 6 shows an embodiment in which a porous solid electrolyte layer 104 is provided on a side of not a first electrode 100 but a second electrode 102. First through fourth electrodes are formed in contact with a single solid electrolyte body.

In Fig. 6, a flat space 110 is a diffusion-resisting means, and a porous ceramic layer 112 is a protective layer for the electrodes as mentioned above. Reference numerals 106, 108, 114, 116 and 118 denote a third electrode, a fourth electrode, a dense solid electrolyte layer, a spacer member, and a lid member, respectively.

Next, examples of the electrochemical elements according to the present invention will be explained.

Example 1

One tenth part by weight of Al₂O₃ are a sintering aid, 2 parts by weight of polyvinyl alcohol as a shaping aid, and water were added and mixed into one hundred parts by weight of a powder consisting of 95 molar % of ZrO₂ and 5 molar % of Y₂O₃, which was pressed to obtain a bottom-closed cylindrical shaped body (giving a dense solid electrolyte body 1 after firing). A slurry consisting of 100 parts by weight of a mixed powder of 70 parts by volume of a powder having 92 molar % of ZrO₂ and 8 molar % of Y₂O₃ and 30 parts by volume of Al₂O₃, 4 parts by weight of polyvinyl alcohol, and water was sprayed onto the outer side of the cylindrical shaped body as a thick film (giving a porous solid electrolyte layer 2 after the firing). Then, a paste containing 95 parts by weight of platinum and 5 parts by weight of powdery zirconia (giving a first electrode 4 after the firing) was coated onto the thick film on the shaped body, which was fired at 1,400 °C for 3 hours. Thereafter, a second electrode 6 was formed on the inner side of the dense solid electrolyte body by non-electrolytic plating with platinum, thereby obtaining an electrochemical element shown in Fig. 1.

The open porosity of the dense solid electrolyte body 1 of the thus obtained electrochemical element was 0.1%, and that of the porous solid electrolyte layer 2 was 3%.

This electrochemical element was compared with two kinds of conventional ones having no porous solid electrolyte layer 2. The conventional electrochemical elements were fired at 1,400 °C and 1,350 °C for 3 hours, respectively, and had the open porosities of 0.1% and 2%, respectively. The element fired at 1,350 °C was not fully fired.

Each of the elements was inserted into propane gas having $\lambda = 0.9$, and the outer side (the first electrode 4) and the inner side (the second electrode 6) were exposed to a propane combustion exhaust gas and air, respectively. The first and second electrodes were connected to a DC potentiometer having an input impedance of 10 M ohms through lead wires, and a potential difference generated between the electrodes was measured. As the temperature of the exhaust gas was gradually lowered from 350 °C, the temperature of the gas at which the potential difference drops to 0.4 V or less was measured. Consequently, the temperatures were 300 °C and 260 °C for the conventional elements fired at 1,400 °C and 1,350 °C, respectively. To the contrary, it was 250 °C for the element according to the present invention. Thus, it was revealed that the element according to the present invention had excellent operability at low temperatures.

Meanwhile, each of these three elements was

inserted into propane gas, and was subjected to a temperature-cycling test (total number of cycling being 500 times) in which each element was maintained at a gas temperature of 900 °C for 30 minutes and at 200 °C for 30 minutes). Consequently, it was revealed that two of three conventional elements fired at 1,350 °C were broken, but none of the conventional elements fired at 1,400 °C and the elements according to the present invention were broken. Thus, it was revealed that the electrochemical elements according to the present invention had sufficient durability.

Example 2

Eight parts by weight of polyvinyl butyral resin and 4 parts by weight of dioctylphthalate as a shaping aid were added and mixed into 100 parts by weight of a powder consisting of 97 molar % of ZrO₂ and 3 molar % of Y₂O₃, which was shaped to form a planar zirconia shaped green body in a thickness of 1 mm according to a doctor blade process (giving a dense solid electrolyte body 40 after firing). A paste containing 50 parts by volume of a powder consisting of 90 molar % of ZrO₂ and 10 molar % of Y₂O₃ and 50 parts by volume of powdery theobromine was coated onto the above zirconia shaped body according to a screen printing process as a thick film of 30 μm in thickness (giving a porous solid electrolyte layer 42 after the firing). Then, a paste containing 95 parts by weight of platinum and 5 parts by weight of zirconia powder was coated onto the thick film (giving a first electrode 44 after the firing) and onto the zirconia shaped body on the side opposite to the thick film (giving a second electrode 46 after the firing).

Then, to the thus obtained laminate structure were piled and press adhered a 0.2 mm thick zirconia shaped green body consisting of 75 parts by volume of a powder of 90 molar % of ZrO₂ and 10 molar % of Y₂O₃ and 25 parts by volume of theobromine powder (giving a porous diffusion layer 48 after the firing) and a 0.2 mm thick zirconia shaped green body consisting of 50 parts by volume of a powder of 90 molar % of ZrO₂ and 10 molar % of theobromine powder (giving a porous diffusion layer 48 after the firing) under heating, which was fired at 1,400 °C to produce an electrochemical element.

As mentioned above, according to the present invention, since the porous solid electrolyte layer is provided through simultaneous firing between at least one of the first and second cermet electrodes and the solid electrolyte body, the invention has the merit that electrochemical elements having excellent response and durability can be obtained.

Claims

1. An electrochemical element comprising a solid electrolyte and a pair of electrodes provided in contact with the solid electrolyte, said solid electrolyte consisting of a dense solid electrolyte body and a porous solid electrolyte layer, and at least one of a pair of said electrodes being a cermet electrode which is formed in contact with the porous solid electrolyte layer when being fired simultaneously with the dense solid electrolyte body and the porous solid electrolyte layer.
2. An electrochemical element according to claim 1, wherein said cermet electrode is substantially exposed to a space for a gas to be measured.
3. An electrochemical element according to claim 1, wherein said cermet electrode is substantially exposed to a space for a reference gas.
4. An electrochemical element according to any one of claims 1 to 3, wherein said pair of the electrodes are both cermet electrodes formed by firing simultaneously with the dense solid electrolyte body and the porous solid electrolyte layer.
5. An electrochemical element according to claim 4, wherein said solid electrolyte consists of a dense solid electrolyte body and first and second porous solid electrolyte layers, said pair of the first and second electrodes being cermet electrodes which are formed in contact with said first and second porous solid electrolyte layers, respectively.
6. An electrochemical element comprising a solid electrolyte, and first and second electrodes provided in contact with the solid electrolyte, the first electrode being exposed, through a diffusion-resisting means having a preset diffusion resistance, to a space for a gas to be measured, said solid electrolyte consisting of a dense solid electrolyte body and a porous solid electrolyte layer, and at least one of said first and second electrodes being a cermet electrode which is formed in contact with the porous solid electrolyte layer when being fired simultaneously with the dense solid electrolyte body and the porous solid electrolyte layer.
7. An electrochemical element according to claim 6, wherein the first electrode is a cermet electrode which is formed in contact with said porous solid electrolyte layer by firing simultaneously with the dense solid electrolyte body and the porous solid electrolyte layer.
8. An electrochemical element according to claim 7, wherein said first and second electrodes are both cermet electrodes which are formed by firing simultaneously with the dense solid electrolyte body and the porous solid electrolyte layer.

9. An electrochemical element according to any one of claims 6 to 8, wherein said diffusion-resistant means is a porous ceramic layer formed by firing simultaneously with the solid electrolyte body.

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10. An electrochemical element according to any one of claims 6 to 9, further comprising a second dense solid electrolyte body, and third and fourth cermet electrodes formed in contact with the second dense solid electrolyte body by firing simultaneously with the second dense solid electrolyte body, wherein said third cermet electrode is exposed to the same gas atmosphere as that of the first cermet electrode.

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11. An electrochemical element according to claim 10, wherein the first and third cermet electrodes are formed by a single common electrode.

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12. An electrochemical element according to claim 10 or 11, wherein said first and second dense solid electrolyte bodies are formed by a single solid electrolyte body.

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FIG. 1

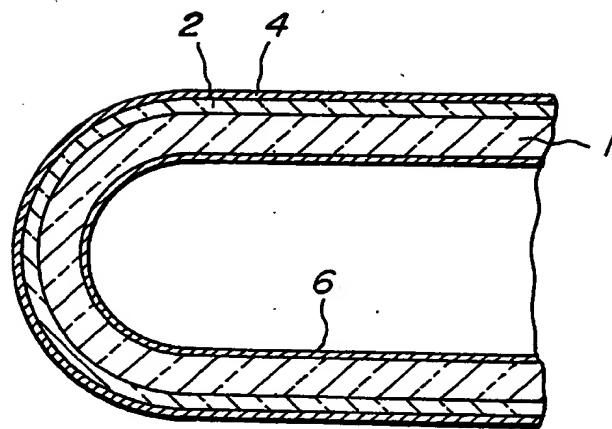
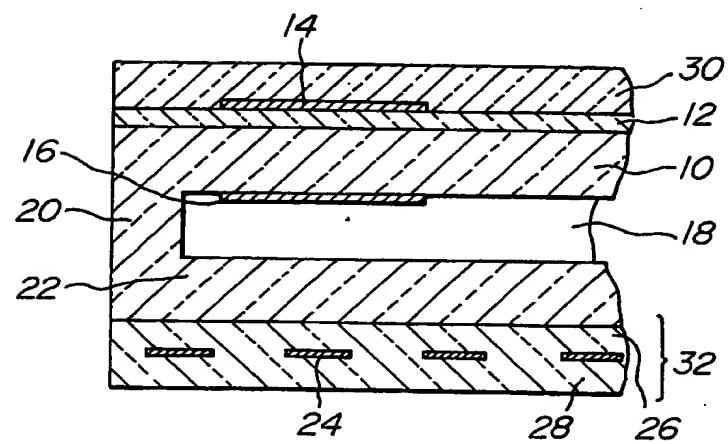
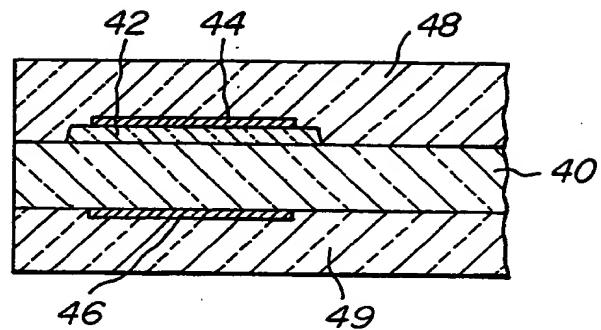


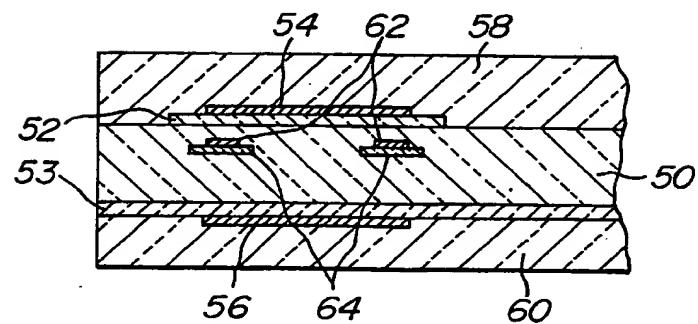
FIG. 2



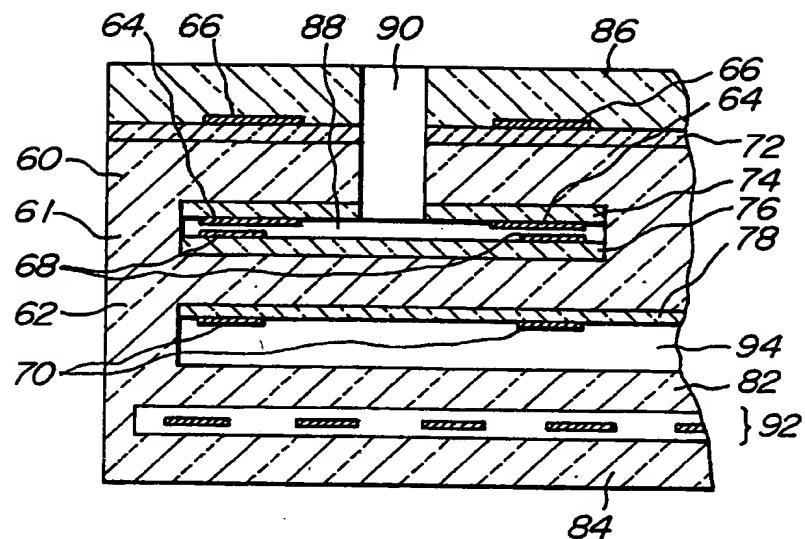
FIG_3



FIG_4



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FIG_5**FIG_6**